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(21) International Application Number: PCT/EP97/00545 (22) International Filing Date: 6 February 1997 (06.02.97) (30) Priority Data: 196 04 238.0 6 February 1996 (06.02.96) DE (71) Applicant (for all designated States except US): ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): STEINKOPF, Bernd [DE/DE]; Marschnerstrasse 3, D-67061 Ludwigshafen (DE). HOLSTEIN, Wolfgang [DE/DE]; Herderstrasse 2, D-35315 Homberg (DE). KATZSCHMANN, Axel [DE/DE]; Helmholtzstrasse 99, D-68723 Schwetzingen (DE). LOHE, Peter [DE/DE]; Ritterstrasse 5, D-67112 Mutterstadt (DE). (74) Agent: KUHNEN, WACKER & PARTNERS; Alois-Steinecker-Strasse 22, D-85354 Freising (DE).		(81) Designated States: AU, CA, CZ, HU, NO, PL, SI, SK, TR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: MINERAL FIBER COMPOSITION (57) Abstract Mineral fiber composition which is decomposable in the physiological medium, characterised by the following constituents in weight percent: SiO ₂ 30 to less than 51; Al ₂ O ₃ higher than 11.5, in particular higher than 13, up to 25; CaO 2 to less than 23; MgO 0 to 15; Na ₂ O + K ₂ O higher than 10, up to 19; TiO ₂ + Fe ₂ O ₃ 6 to 18; various 0 to 3.		

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Description

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Mineral fiber composition

The present invention relates to a mineral fiber composition which is highly decomposable in the physiological medium.

The prior art describes several mineral fiber compositions which are specified to be decomposable in a physiological environment.

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Physiological decomposition of mineral fiber compositions is of great significance inasmuch as various investigations point out that certain mineral fibers having very small diameters in the range of less than 3 μm are suspected of being carcinogenic, whereas mineral fibers of such dimensions which are physiologically well decomposable do not show any carcinogenicity.

The mineral fiber compositions do, however, also have to have good processing properties with known methods for manufacturing small-diameter mineral wool, in particular the blast drawing method. This means particularly a sufficient processing range of e.g. 80°C and suitable viscosity of the molten material.

In addition, the mechanical and thermal properties of the mineral fibers and of the respective products produced therefrom are of decisive importance. Mineral fibers are for instance utilised in a large scope for

insulation purposes. Especially for utilisation in the industrial sector and for fire protection elements, the mineral fibers need to have sufficient heat stability.

5 It is the object of the invention to create a new mineral fiber composition which is distinguished by a high degree of physiological decomposability, shows good heat stability, has good processing properties, and can be produced economically.

10

 The invention is based on the insight that this object may be achieved by specific mineral fiber compositions made up of silicon dioxide and alkaline earth oxides, and furthermore have a relatively high content of sodium oxide and/or potassium oxide and a substantial content of alumina as well as titanium oxide and/or iron oxide.

20 It was found that such mineral fiber compositions satisfy the combination of required properties, as there are a high degree of physiological decomposability, sufficient heat stability for insulation purposes in the industrial sector, and good processing properties in manufacturing the mineral wool proper and the products. This also includes the condition that the upper devitrification temperature of the molten material is preferably lower than 1,300°C. The mean fiber diameter is preferably 4 to 5 μm or less.

30 The subject matter of the invention is a mineral fiber composition which has a high degree of decomposability in the physiological medium and which is characterised by the following constituents in weight per cent:

	SiO ₂	30 to less than 51
	Al ₂ O ₃	higher than 11.5; in particular higher than 13, up to 25
5	CaO	2 to less than 23
	MgO	0 to 15
	Na ₂ O + K ₂ O	higher than 10 to 19
	TiO ₂ + Fe ₂ O ₃	6 to 18
	Various	0 to 3

10

What is referred to by Fe₂O₃ in this context are the contents of Fe₂O₃ and of FeO (expressed as Fe₂O₃).

15 In preferred embodiments of the invention, the Al₂O₃ content is around 14.2% (wt.), 14.5% (wt.) or 17.1% (wt.) as concentration values, or as minimum values of the concentration range up to 25% (wt.).

20 The concentration of Na₂O + K₂O preferably amounts to 10.4% (wt.) or 12% (wt.) as concentration values, or as minimum values of the concentration range up to 19% (wt.).

25 The mineral fiber compositions of the invention in particular can be well attenuated by the blast drawing method, which means that a mineral wool having good fineness and a low bead content is obtained.

30 Such mineral fibers attain high heat stability and may also be used for fire protection structures having a resistance rating of at least 90 minutes which was determined in the so-called small-flame furnace according to DIN (German Industrial Standard) 4102, Part 17. Furthermore the limit temperatures of application as

determined according to AGQ 132 for the industrial sector are higher than 600°C.

5 Although the relatively high proportion of sodium oxide and/or potassium oxide results in a lowered melting point and thus in better processing properties in the melting and fiberising processes, the wool nevertheless surprisingly has a high heat stability.

10 For obtaining the above specified properties, it is advantageous that the contents of alkali oxides and alumina have a molar ratio of

$$(Na_2O + K_2O) : Al_2O_3 < 1:1,$$

15

preferably a molar ratio of 1:1.

This molar ratio roughly corresponds to a weight proportion of alkali oxides and alumina of
20 $\leq 0,7:1$.

The mineral fiber compositions according to the invention preferably may be melted in melting tubs fired by fossile fuels, in particular natural gas, at
25 melting temperatures of 1,350 to 1,450°C. Such melting tubs are suited for obtaining a homogeneous molten material, which is a precondition for consistent product quality. Homogeneity of the molten glass material also facilitates reproduceability of the fiberisation
30 process and thus of the thermal and mechanical product properties. Moreover the chemical composition of the mineral wool thus produced results in a consistently high degree of physiological decomposability.

In particular the addition of alumina, titanium oxide and iron oxide increases the heat stability of the mineral wool.

- 5 Preferably the mineral fiber compositions of the invention have the following constituents in weight per cent:

	SiO ₂	30 to less than 47
10	Al ₂ O ₃	higher than 11.5; in particular higher than 13, up to 24
	CaO	4 to 20
	MgO	0 to 15
	Na ₂ O + K ₂ O	higher than 10, up to 18
15	TiO ₂ + Fe ₂ O ₃	7 to 16
	Various	0 to 2

- 20 In particular the mineral fiber compositions of the invention include the following constituents in weight per cent:

	SiO ₂	35 to 45
	Al ₂ O ₃	higher than 12, up to 20
25	CaO	8 to 17.5
	MgO	2 to 10
	Na ₂ O + K ₂ O	higher than 10, up to 16
	TiO ₂ + Fe ₂ O ₃	7 to 15
	Various	0 to 2

30

The aluminum content of the composition is preferably between 13 and 20% (wt.).

The physiological decomposability of mineral fibers was determined in animal, i.e. *in-vivo* experiments by the so-called intratracheal test. Herefor the fibers to be tested were injected via the trachea into the bronchial system of the lungs of test animals (rats) by means of one or several injections. In rats as well as in human beings, particles which have penetrated into the lungs are decomposed physiologically by various defense mechanisms, e.g. macrophages, or chemical attack by lung fluid. At predetermined points of time, as a rule 35 animals are killed and the number of fibers, i.e. of non-decomposed fibers, inside the lungs is determined.

This serves to determine how quickly the fibers are decomposed inside the lungs. Based on the development over time and by approved mathematical methods, one determines the half-life period of the fiber, i.e. the time period in which 50% of the fibers inside the lungs are decomposed. A lower half-life corresponds to a higher degree of physiological decomposability of the fiber. Thus the so-called Bayer B-01 fiber has a mean half-life of 32 days in the intratracheal test.

In analogy with this B-01 mineral fiber, other mineral fibers were examined as well, which had half-life values in a range of less than 50 days and were rated to be non-carcinogenic.

The physiological decomposability of the mineral fibers according to the invention even reached values which were clearly lower than 50 days, in particular a half-life of less than 40 days. These values rule out carcinogenicity.

The temperature behavior of the mineral fibers was determined in a small-flame furnace as specified by DIN 4102, Part 17, Determination of limit temperature of application.

The invention shall be described in more detail below by reference to exemplary embodiments.

10

Example 1

A mineral wool having the following composition in weight per cent was produced.

15

	SiO ₂	41.3
	Al ₂ O ₃	18.4
	CaO	15.0
	MgO	7.6
20	Na ₂ O	9.5
	K ₂ O	1.3
	TiO ₂	1.1
	Fe ₂ O ₃	5.6

25

By using the blast drawing method and at an attenuating temperature between 1,300 and 1,400°C, this composition could readily be processed into mineral fibers having a mean diameter of 4,5 µm.

30

The wool met the conditions for the melting point test at 1,000°C.

Example 2

A mineral wool having the following composition in weight per cent was produced:

5

	SiO ₂	39.3
	Al ₂ O ₃	18.3
	CaO	18.4
	MgO	6.6
10	Na ₂ O	4.5
	K ₂ O	6.2
	TiO ₂	0.4
	Fe ₂ O ₃	6.1

15

By using the blast drawing method and at an attenuating temperature between 1,300 and 1,400°C, this composition could readily be processed into mineral fibers having a mean diameter of 4.5 to 5 µm.

20

Example 3

A mineral wool having the following composition in weight per cent was produced:

25

	SiO ₂	44.0
	Al ₂ O ₃	18.5
	CaO	13.0
	MgO	5.2
30	Na ₂ O	6.6
	K ₂ O	5.9
	TiO ₂	0.4
	Fe ₂ O ₃	6.2

By using the blast drawing method and at an attenuating temperature between 1,300 and 1,400°C, this composition could also readily be processed into mineral fibers having a mean diameter of 5.5 μm .

5

Example 4

A mineral wool having the following composition in
10 weight per cent was produced:

	SiO_2	37.4
	Al_2O_3	22.2
	CaO	17.2
15	MgO	5.7
	Na_2O	4.5
	K_2O	6.2
	TiO_2	0.5
20	Fe_2O_3	6.1

Example 5

A mineral wool having the following composition in
25 weight per cent was produced:

	SiO_2	43.9
	Al_2O_3	15.2
	CaO	17.4
30	MgO	6.6
	Na_2O	4.5
	K_2O	6.2
	TiO_2	0.2
	Fe_2O_3	6.0

Example 6

A mineral wool having the following composition in
5 weight per cent was produced:

10	SiO ₂	42.6
	Al ₂ O ₃	17.9
	CaO	15.0
	MgO	7.3
	Na ₂ O	4.4
	K ₂ O	6.1
	TiO ₂	0.4
	Fe ₂ O ₃	6.3

Claims

- 5 1. Mineral fiber composition which is decomposable in the physiological medium, characterised by the following constituents in weight per cent:
- | | | |
|----|---|--|
| 10 | SiO ₂ | 30 to less than 51 |
| | Al ₂ O ₃ | higher than 11.5; in particular higher than 13, up to 25 |
| | CaO | 2 to less than 23 |
| | MgO | 0 to 15 |
| | Na ₂ O + K ₂ O | higher than 10 to 19 |
| 15 | TiO ₂ + Fe ₂ O ₃ | 6 to 18 |
| | Various | 0 to 3 |
- 20 2. Mineral fiber composition according to claim 1, characterised by the following constituents in weight per cent:
- | | | |
|----|---|--|
| 25 | SiO ₂ | 30 to less than 47 |
| | Al ₂ O ₃ | higher than 11.5; in particular higher than 13, up to 24 |
| | CaO | 4 to 20 |
| | MgO | 0 to 15 |
| | Na ₂ O + K ₂ O | higher than 10, up to 18 |
| | TiO ₂ + Fe ₂ O ₃ | 7 to 16 |
| 30 | Various | 0 to 2 |

3. Mineral fiber composition according to claim 1 or 2, characterised by the following constituents in weight per cent:

5	SiO ₂	35 to 45
	Al ₂ O ₃	higher than 14, up to 20
	CaO	8 to 17.5
	MgO	2 to 10
	Na ₂ O + K ₂ O	higher than 10, up to 16
10	TiO ₂ + Fe ₂ O ₃	7 to 15
	Various	0 to 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/00545

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 14274 A (ROCKWOOL INT ;JENSEN SOREN LUND (DK); CHRISTENSEN VERMUND RUST (DK) 17 May 1996 see page 4, line 7 - page 5, line 3 see page 6, line 35 - page 8, line 29; table ---	1-3
A	EP 0 583 791 A (SAINT GOBAIN ISOVER) 23 February 1994 see page 10; table see page 17 - page 18; table ---	1-3
A	EP 0 009 418 A (PARTEK AB) 2 April 1980 see page 4, line 33 - page 5, line 22; examples --- -/--	1-3

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☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 83 01947 A (US ARMY) 9 June 1983 see page 1, last paragraph - page 2, paragraph 2; table I ---	1-3
A	PL 160 196 A (CENTRALNY OSRODEK BADAWCZO-ROZWOJOWY PRZEMYSŁU IZOLACJI BUDOWLANEJ) 26 February 1993 see the whole document -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 97/00545

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9614274 A	17-05-96	AU 3871595 A	31-05-96
		AU 3871695 A	31-05-96
		BE 1009073 A	05-11-96
		DE 29515168 U	14-03-96
		WO 9614454 A	17-05-96
		FR 2726548 A	10-05-96
		NL 1001607 C	10-12-96
		NL 1001607 A	21-08-96

EP 0583791 A	23-02-94	CA 2121572 A	03-03-94
		WO 9404468 A	03-03-94
		AU 2433192 A	15-03-94
		BR 9206653 A	24-10-95
		CN 1087611 A	08-06-94
		FI 941816 A	20-04-94
		JP 7503696 T	20-04-95
		NO 941403 A	18-04-94
		NZ 248380 A	21-12-95
		SI 9300437 A	31-03-94
		SK 45594 A	07-09-94
		AU 668878 B	23-05-96
		HR 931148 A	30-06-96
		US 5554324 A	10-09-96

EP 0009418 A	02-04-80	JP 55047246 A	03-04-80

WO 8301947 A	09-06-83	EP 0095490 A	07-12-83

PL 160196 A		NONE	
